



JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

# ACCEPTED MANUSCRIPT

This is an early electronic version of an as-received manuscript that has been accepted for publication in the Journal of the Serbian Chemical Society but has not yet been subjected to the editing process and publishing procedure applied by the JSCS Editorial Office.

Please cite this article as F. Mustafayeva, N. Kakhramanov, G. Martynova, and N. Koseva, *J. Serb. Chem. Soc.* (2025) <u>https://doi.org/10.2298/JSC241112021M</u>

This "raw" version of the manuscript is being provided to the authors and readers for their technical service. It must be stressed that the manuscript still has to be subjected to copyediting, typesetting, English grammar and syntax corrections, professional editing and authors' review of the galley proof before it is published in its final form. Please note that during these publishing processes, many errors may emerge which could affect the final content of the manuscript and all legal disclaimers applied according to the policies of the Journal.



JSCS-13115



JSCS-info@shd.org.rs • www.shd.org.rs/JSCS Original scientific paper Published DD MM, 2025

# Effect of different compatibilizers and aluminium hydroxide amount on the thermophysical and thermomechanical properties of polypropylene random copolymer / aluminium hydroxide composites

FATIMA MUSTAFAYEVA<sup>1\*</sup>, NAJAF KAKHRAMANOV<sup>1</sup>, GALINA MARTYNOVA<sup>2</sup> AND NELI KOSEVA<sup>3</sup>

<sup>1</sup>Institute of Polymer Materials of Ministry of Science and Education Republic of Azerbaijan, S. Vurgun Str. 124, Sumgait, Republic of Azerbaijan, <sup>2</sup>Institute of Geology and Geophysics of Ministry of Science and Education Republic of Azerbaijan, H. Javid av. 119, Baku, Republic of Azerbaijan, and <sup>3</sup>Institute of Polymers, Bulgarian Academy of Sciences, ul. "Akad. Georgi Bonchev" 103, 1113 Geo Milev, Sofia, Bulgaria.

(Received 12 December 2024; revised 3 February 2025; accepted 19 March 2025)

Abstract: This study investigates the effects of three different types of commercial available compatibilizers (DuPont<sup>TM</sup> Fusabond<sup>®</sup> P353 Polymer Modifier, Exxelor<sup>TM</sup> PO 1020, LIBAID T-2) on the thermal properties of composites based on polypropylene random copolymer / aluminium hydroxide (PP-R/ATH). The influence of the above-mentioned compatibilizers and the ATH amount on the thermophysical and thermomechanical properties of composites based on PP-R/ATH is considered. Thermal properties of the obtained composites were analyzed using differential scanning calorimetry, thermogravimetric analysis, derivative thermogravimetry and thermomechanical curves. The results of the study show that the content of ATH in the PP-R matrix in the presence of a compatibilizer and without it has a noticeable effect on the regularities of changes in thermophysical and thermomechanical characteristics. With increasing filler content, an increase in the amount of residue corresponding to 700 °C, temperature at the maximum mass loss rate, 50% decomposition temperature, and a decrease in temperature at onset degradation were observed. The effect of the used compatibilizer was not significant to the melting temperature at low amount (5 wt. %) of ATH, however, different results were obtained for high amounts (50 wt. %) of filler. Composites with compatibilizer had lower melting enthalpies than those without compatibilizer.

*Keywords:* polypropylene random copolymer; aluminium hydroxide; compatibilizer; maleic anhydride functionalized polypropylene copolymer; maleic anhydride functionalized homopolypropylene; blend of fatty acid metal soap and amide; melting temperature; decomposition temperature.

<sup>\*</sup> Corresponding author. E-mail: <u>mustafayevafatima@mail.ru</u>, <u>F.A.Mustafayeva@gmail.com</u> <u>https://doi.org/10.2298/JSC241112021M</u>

# 0

#### MUSTAFAYEVA et al

# INTRODUCTION

As is known, one of the main disadvantages of polymeric materials is their high flammability. Being organic in nature, polymeric materials used in various fields of engineering and technology are materials that are prone to combustion and fire spread, leading to loss of life and material damage. In this regard, the obtain of fire resistant polymer composite materials with improved physical and mechanical properties is a priority task in the field of materials science. As a matrix material, polypropylene (PP) is the most promising material due to its relatively high melting point, low cost, good physical and mechanical properties, and ease of processing by injection molding, extrusion, vacuum-pneumatic molding, etc. PP based composites are widely used in many areas of industry: aircraft manufacturing, automotive manufacturing, shipbuilding, electronics, military and space technology, etc. PP, the production volume of which is continuously increasing, is one of the most produced and consumed polymers in the world.<sup>1</sup> At the same time, the main disadvantage of using PP for special purposes is their flammability. In addition, PP forms molten droplets when burned and releases a large amount of heat and toxic gases. Therefore, improving the flame retardant properties of the polyolefin under consideration (polypropylene random copolymer) is an important research task.<sup>2, 3</sup>

The use of flame retardants is a simple and effective way to reduce the fire hazard of polymers. In this case, aluminium hydroxide (ATH) has many advantages over halogen-based flame retardants, including environmental friendliness, low cost, smoke suppression, low toxicity, minimization of melt droplet formation, and low corrosion.<sup>4-6</sup> Therefore, considering the environmental benefits, ATH is widely used as a flame retardant and is one of the main reasons for its increasing practical use every year. ATH is one of the most commonly used retardants, making up approximately 34-40 % of the total flame retardants used worldwide.<sup>7</sup> It is generally believed that ATH in polymeric materials performs a triple function: filler, flame retardant, and smoke extinguisher.<sup>8</sup> Endothermic decomposition of ATH general occurs within the temperature range of 220-300 °C and the enthalpy of water release is  $1.17 \text{ kJg}^{-1}$  for it:<sup>9</sup> 2Al(OH)<sub>3</sub>  $\rightarrow$  Al<sub>2</sub>O<sub>3</sub> + 3H<sub>2</sub>O.

This endothermicity is certainly part of the mode of action of ATH. Water produced during decomposition both cool the substrate surface, and dilutes flammable gases that are expelled from the thermally decomposing substrate. The  $Al_2O_3$  that remains in the substrate acts as a heat sink, and also reduces the further release of low molecular weight volatiles.<sup>7</sup> The effectiveness of ATH on flame retardant properties is directly proportional to its content in the polymer composite. So, for example, to achieve sufficient flame retardant properties of a material, it is necessary to use it in the composition of a polymer matrix in an amount of approximately 50-60 wt. %. However, such a high degree of filling has a negative





impact on the change in the physical and mechanical characteristics of the composites.

The dispersion of fillers and their compatibility with the polymer matrix are the main factors that determine the high quality characteristics of composite materials. Therefore, in the world, a lot of attention has been paid to problems related to the development and study of the properties of composites based on PP/ATH.<sup>10-12</sup> The PP/ATH composite was found to be more fire resistant as compared to pure PP.<sup>13</sup> Parida and co-authors used MAPP to improve the compatibility between PP and ATH and found that with increasing amounts of ATH of different sizes (nano or micro), the flame retardant properties of the composite increased, while the tensile strength and elongation at break decreased. <sup>14</sup> Noorasikin et al studied the effect of two different types of coupling agent (3aminopropyltriethoxysilane and maleic anhdridegraftted polyproplene) on the flame retardant properties of PP/ATH-based nanocomposites and showed that the type of coupling agents affects fire retardancy.<sup>15</sup> Many studies have also shown that the addition of a compatibilizer can improves the thermal properties of composites <sup>16, 17</sup>, increases their thermal stability <sup>18</sup>, onset decomposition temperature <sup>19</sup>, final decomposition temperature <sup>20</sup> and reduces mass loss <sup>20</sup>.

Based on the above, the main objective of this work was to study the influence of the type of commercial grade compatibilizer and amount of ATH on the thermophysical and thermomechanical properties of composite materials, including the determination of their softening temperature, melting temperature, and decomposition temperature.

### EXPERIMENTAL

### Materials

The polypropylene used was polypropylene random copolymer (PP-R) Topilene<sup>®</sup> R200P (HYOSUNG CHEMICAL CORPORATION), with a melt index of 0.2 g/10 min (temperature = 230 °C, load = 2.16 kg) and 0.90 g/cm<sup>3</sup> density. The ATH was used (repackaged by ZAO VEKTON, OKP 931887, GOST 11841-76), finely ground in A-11 basic (IKA, Germany) brand analytical mill. ATH with average particle size of 56 nm (Dv (10) =0.0197 $\mu$ m; Dv (50) =0.0559 $\mu$ m; Dv (90) =0.159 $\mu$ m)) was used. Size determination of filler particles was carried out on a Mastersizer 3000 (Malvern Instruments, England) laser analyzer with a measurement range of 10 nm to 3500  $\mu$ m.

Three kind of compatibilizer were used to compatibilize PP-R/ATH blend. The first compatibilizer used was DuPont<sup>TM</sup> Fusabond<sup>®</sup> P353 Polymer Modifier (DuPont Company) – polypropylene copolymer grafted with maleic anhydride (PPC-g-MAH), MAH grafting degree 1.3-1.9 %. Physical properties: 0.904 g/cm<sup>3</sup>, 22.4 g/10 min melt flow index (160 °C / 325 g). Thermal properties: 135 °C melting point, 112 °C Vicat softening point.

The second compatibilizer used was maleic anhydride functionalized homopolypropylene (PPH-g-MAH) – Exxelor<sup>TM</sup> PO 1020 Polymer Resin (ExxonMobil Chemical Company), maleic anhydride level is in the range of 0.5 to 1.0 wt.%. This grade is designed to function as a coupling agent between reinforcing materials, such as inorganic fillers and polypropylene.





Physical properties: 0.900 g/cm<sup>3</sup>, 430 g/10 min melt flow index (230 °C / 2.16 kg). Thermal properties: 162 °C peak melting temperature.

The third used coupling agent was blend of fatty acid metal soap and amide – LIBAID T-2 (Liberty Chemicals). Specification: 100-105 °C melting point, > 300 °C flash point. It is unique processing aid developed for applications where filler need to be dispersed uniformly in polymer matrix. LIBAID T-2 has sites available for hydrogen bonding and is therefore able to act as a physical coupling agent between polymer systems and a range of filler materials. This permits LIBAID T-2 to act as an efficient blending or dispersing agent in highly filled systems, providing a more uniform and homogenous initial mix.

The dosage of a compatibilizers is based on the results of our previous research results and also on the supplier recommendations.<sup>21,22</sup> Table I lists the amounts of components in each sample.

#### Preparation of the studied composites

Compositions based on PP-R and ATH at various content of ATH were prepared without and with the use of a compatibilizer. All composites were obtained by mixing  $Al(OH)_3$  in a melt on hot rollers at a temperature of 170 °C for 10 minutes. The resulting composite was subjected to pressing at a temperature of 180 °C, followed by cooling to 50 °C under a pressure of 100 MPa. Blades were cut from the obtained sheets to study the physical and mechanical properties of the composites.

#### Characterization

Differential Scanning Calorimetry (DSC). DSC of samples was performed using STA 6000 Simultaneous Thermal Analyzer, by Perkin Elmer. The rate change in temperature was constant at 10 °C/min.

Thermogravimetric Analysis (TGA). The thermogravimetric analysis of the samples was performed using the STA 6000 Simultaneous Thermal Analyzer (Perkin Elmer) at temperature range of 25–700 °C under nitrogen atmosphere with 50 mL/min flow rate, a heating rate of 10 °C/min.

Thermomechanical Properties. The thermomechanical properties of the samples were determined using a Kanavets instrument. The deformation was measured at successively changing temperatures (T) at a load of 0.5 kg/cm<sup>2</sup> and a heating rate of 50 °C/h. To carry out research, tablets 24 mm in diameter, 6 mm high and weighing 3.5-4 g with a smooth surface were pressed in a special mold. Based on the experimental data obtained, thermomechanical curves  $\Delta = f(T)$  of the dependence of polymer composites were constructed.



THERMOPHYSICAL AND THERMOMECHANICAL PROPERTIES OF COPOLYMER

	Committe en de	PP-R	ATH	Compatibilizer (wt.%)		
	Sample code	(wt.%)	(wt.%)	PPC-g-MAH	PPH-g-MAH	LIBAID T-2
	PP-R	100	-	-	-	
	$PA_1$	99	1	-	-	_
	PA <sub>3</sub>	97	3	-	-	
	PA <sub>5</sub>	95	5	-	-	
	$PA_{10}$	90	10	-	-	-
	PA20	80	20	-	-	-
	PA30	70	30	-	-	-
	PA50	50	50	-	-	-
	PC	97	-	3	-	-
	$PCA_1$	96	1	3	-	-
	PCA <sub>3</sub>	94	3	3	-	-
	PCA <sub>5</sub>	92	5	3		-
	PCA <sub>10</sub>	87	10	3	-	-
	PCA <sub>20</sub>	77	20	3	-	-
	PCA <sub>30</sub>	67	30	3	-	-
	PCA <sub>50</sub>	47	50	3	-	-
	PH	98	-	-	2	-
	$PHA_1$	97	1	-	2	-
	PHA <sub>3</sub>	95	3	-	2	-
	PHA <sub>5</sub>	93	5	-	2	-
	$PHA_{10}$	88	10	-	2	-
	PHA <sub>20</sub>	78	20	-	2	-
	PHA <sub>30</sub>	68	30	-	2	-
	PHA <sub>50</sub>	48	50	-	2	-
	PL	99	-	-	-	1
	PLA <sub>1</sub>	98	1	-	-	1
	PLA <sub>3</sub>	96	3	-	-	1
	PLA <sub>5</sub>	94	5	-	-	1
	PLA <sub>10</sub>	89	10	-	-	1
	PLA <sub>20</sub>	79	20	-	-	1
	PLA <sub>30</sub>	69	30	-	-	1
	PLA <sub>50</sub>	49	50	-	-	1

TABLE I. Identification and formulations of all prepared samples

# RESULT AND DISCUSSION

The thermal performance of composites was determined via TGA, derivative thermogravimetry (DTG), DSC, and thermomechanics.

Resistance to thermal degradation of polymeric materials is an important parameter, since it determines the thermal stability of polymer composite materials and allows determining their temperature range of processing and application in various operating conditions. TGA was carried out to determine the influence of the choice of the compatibilizer type and ATH amount on the thermal stability of the samples. Fig. 1 shows the TGA diagrams for initial components (PP-R,

Al(OH)<sub>3</sub>), PP-R/ATH composites and for the composites in the presence of a compatibilizer (PP-R/ compatibilizer /ATH) at different Al(OH)<sub>3</sub> contents.

As can be seen from this figure, the decomposition of the initial filler ATH begins at 234 °C and is accompanied by a mass loss of 34.661 wt. % due to decomposition and the release of water vapor from its composition. The resulting residue based on  $Al_2O_3$  is approximately 65.339 wt. %. On the other hand, pure PP-R undergoes thermal destruction at a temperature of 345 °C and continues up to 475 °C, leaving a residue of 0.343 wt. %.

In the case of PP-R/ATH composites with and without compatibilizer, they present very similar curves that are superimposed on each other. As expected from the analysis of the TGA results of polymer composites, the used compatibilizer has virtually no effect on the thermal stability of the resulting composites. This circumstance indicates that the action of the compatibilizer manifests itself only in the solid state and in the melt of the composite, i.e. up to the temperature of thermal destruction.



Fig. 1. TGA curves of composites based on PP-R/ATH

The decomposition of PP-R/ATH based composites filled with Al(OH)<sub>3</sub> is one of the complex thermal processes, especially at its initial stage. According to the TGA data in Fig. 1, the decomposition process begins at lower temperatures. A TGA study of the composites showed that their thermal stability depends on the ATH content. The initial decomposition temperature (weight loss of 1.266 %) of PA<sub>5</sub> was around 318 °C, which was much lower than that of pure PP-R.

7 on

Furthermore, with the addition of a compatibilizer, the initial decomposition temperatures of the compatibilized blends were all increased. This circumstance allows us to assert that physical bonding of the compatibilizer to the polymer matrix can contribute to an increase in the initial stage of thermal stability.<sup>23</sup>

Table II shows the effect of filler content on the melting temperature  $(T_m)$  and temperature characteristics of thermal decomposition of composites and the content of residue at 700 °C. According to the data in this table, the addition of flame retardant filler (Al(OH)<sub>3</sub>) improved the thermal stability of the composites.

PP-R exhibits one stage of rapid thermal decomposition. The composites containing 5 wt. % ATH exhibit one main mass loss stage, while the composites containing 50 wt. % ATH showed two mass losses stage (Fig. 1). The thermogram of samples with 50 wt. % ATH is represented by a complex multi-stage decomposition curve, consisting of 2 main sections. The first decomposition area was attributed to the loss of removal of water from ATH. The second region of thermal decomposition corresponded to the decomposition of the polymer matrix itself.

	Sample code	$T_{\rm m}$	$T_{onset}$	$T_{50\%}$	$T_{max}$	Residue at 700°C
_	-	$(\mathbf{C})$	$(\mathbf{C})$	$(\mathbf{C})$	$(\mathbf{C})$	(WL 70)
	ATH		234.34	_	294.70	65.339
	PP-R	145.36	345.32	451.48	451.48	0.343
	PA <sub>5</sub>	146.69	318.25	441.19	441.19	2.381
	PCA <sub>5</sub>	146.19	330.56	446.17	446.17	3.035
	PHA <sub>5</sub>	149.33	336.52	446.44	446.44	3.092
	PLA <sub>5</sub>	146.40	341.07	446.96	446.96	3.926
	PA <sub>50</sub>	146.67	246.72	449.30	461.40	32.722
	PCA <sub>50</sub>	137.77, 204.63	246.46	461.35	461.35	34.564
	PHA <sub>50</sub>	138.90	247.93	461.97	461.97	32.653
	PLA <sub>50</sub>	147.04	247.03	461.45	461.45	32.756
-						

TABLE II. Thermal properties of composites based on PP-R/ATH

 $T_{50\%}$  – 50% decomposition temperature;  $T_{max}$  – temperature of maximum decomposition rate

Early decomposition of ATH in PP-R/ATH and PP-R/ compatibilizer /ATH composites is due to the endothermic dehydration of Al(OH)<sub>3</sub> at about 234 °C. The onset temperature degradation values of the composites containing ATH shifted to lower temperatures. The onset thermal destruction of composites with 5 wt. % content of ATH varies within the range of 10-20°, and with an ATH content of 50 wt. % within the range of 1°. The temperature for maximum rate of thermal destruction corresponding to the peak in the DTG plot is also maintained around the value of 446 °C for PCA<sub>5</sub>, PHA<sub>5</sub>, PLA<sub>5</sub> and 461°C for PA<sub>50</sub>, PCA<sub>50</sub>, PHA<sub>50</sub>, PLA<sub>50</sub>. This confirms the independence of the thermal decomposition process from the degree of dispersion as well as polymer-filler interaction.





Onset decomposition temperature of the PP-R/ATH composite is lower than that of PP-R due to early decomposition of ATH. The use of compatibilizers with PP-R/ATH leads to an increase in  $T_{onset}$ . The temperature of 50% weight loss ( $T_{50\%}$ ) of the PP-R/ compatibilizer / 50 wt. % ATH of higher than that on PP-R, and the use of compatibilizers produces no significant change in  $T_{50\%}$ .

The obtained results show that with an increase in the amount of ATH in the composite, there is an increase in the residue due to the formation of aluminium oxide. This fact indicates that the flame retardant additive  $(Al(OH)_3)$  creates an effective barrier layer that limits heat transfer into the internal volume of the polymer matrix, thereby reducing the rate of mass loss of the composites.<sup>24</sup> Al<sub>2</sub>O<sub>3</sub> has a melting point of 2852 °C, which confirms its extremely high heat resistance. There is reason to believe that the decomposition product  $(Al_2O_3)$ , contribute to a significant inhibition of the process of thermal decomposition of PP-R.<sup>25</sup>

Experimentally measured derivative thermogravimetric (DTG) curves of initial PP-R, ATH and composites based on them with different compatibilizer and ATH content are presented in Fig. 2. From the DTG data, it could be found that the pure PP-R had the largest thermal weight loss rate of 25.715 % min<sup>-1</sup> at 451.48 °C, while which of the PCA<sub>50</sub>, PHA<sub>50</sub>, PLA<sub>50</sub>, composites was only about 15.264 % min<sup>-1</sup>, 15.721 % min<sup>-1</sup>, 14.543 % min<sup>-1</sup> at the temperature 461.35 °C, 461.97 °C and 461.45 °C respectively indicating that the addition of ATH retarded the thermal degradation rate of polymer and increased the thermal stability of polymer. Thus, the above thermal analysis results showed that the introduction of ATH into PP-R resulted in lower maximum weight loss rate and higher residue (Table II) which suggested an increase of the thermal stability.<sup>26</sup> The addition of a compatibilizer improves dispersion of the filler particles, which results in a noticeable improvement in the thermal stability of PP-R.<sup>17</sup>

DSC curves are shown in Fig. 3. DSC was performed to understand the thermal properties of composites containing various compatibilizers and to evaluate the influence of ATH loading on the crystallite melting pattern. The  $T_m$  of PP-R/ATH based composites are tabulated in Table II. Based on DSC data, we can say that the introduction of 5 wt. % ATH into PP-R with and without compatibilizers slightly affect the melting onset temperature; i.e. the melting peak temperature increased from 145 °C for PP-R to 146 °C. This increase in melting temperature can be explained by the effect of a heterogeneous nucleation center, which makes it possible to obtain polymer composites with a fine-spherulitic supramolecular structure.<sup>27</sup> At 50 wt. % ATH, a slight shift in the melting temperature towards lower temperatures is observed, which may be associated with the formation of simple rod-shaped crystals, which affect the decrease in their melting temperature. The nucleation effect is effective at low amount (5 wt. %) of ATH. At a higher amount (50 wt.%), the simultaneous formation of a large number of



THERMOPHYSICAL AND THERMOMECHANICAL PROPERTIES OF COPOLYMER

9





Fig. 2. DTG curves of composites based of PP-R/ATH

During melting, ATH particles and the PP-R matrix are subject to the same thermal flow. At a lower ATH content (5 wt.%), this amount of thermal energy is quite sufficient for the decomposition of ATH. At a high ATH content (50 wt.%) relative to the PP-R matrix, the decomposition process slows down due to the shielding of the thermal effect by a large number of ATH particles, which leads to higher thermal stability of the composite. If we analyze the influence of the compatibilizer, we can establish that in its presence the enthalpy of melting of the

composites becomes comparatively lower. This effect can be associated with an increase in the adhesive contact between the surface of the filler particles and the macrochains of the polymer matrix.





As can be seen from the data presented in Fig. 3 and in Table II, in contrast to the other samples, two melting peaks were observed for the PCA<sub>50</sub> composite. In all likelihood, the appearance of two melting peaks may be the result of sequential polymorphism. In other words, this can be interpreted as the fact that the supramolecular structure of the composite is formed by polystructural formations with varying degrees of perfection of the crystalline phase.<sup>29</sup>

It is known that polymeric materials are characterized by a significant dependence of mechanical properties on temperature, which is determined by the structural features of high-molecular compounds. Therefore, the problem of studying the deformation characteristics of polymers depending on temperature is one of the important features of the thermomechanical behavior of polymers. The results of these studies are very useful in assessing the processing capabilities of polymers into products. Using thermomechanical curves, it is possible to estimate the first-order phase transition (softening temperature), as well as the behavior of composites in solid, highly elastic and viscous-flow states. Thermomechanical analysis allows us to establish the nature of the change in temperature transition from one physical state to another, which provides important information when choosing the modes of processing and operation of these materials. The obtained



11

experimental data are presented in Fig. 4 (a, b, c, d) in the form of thermomechanical curves showing the dependence of deformation on temperature depending on the ATH content.



Fig. 4. The influence of ATH content on thermomechanical curves of the dependence of deformation on temperature

From a comparative analysis of the curves in these figures, it can be seen that the presented thermomechanical curves have practically the same regularity of changes in deformation from temperature. The difference is manifested in the change in phase transition temperature. Above softening temperatures, intensive development of deformation is observed, associated with the melting of the crystalline phase of the polymer matrix and its transition to a viscous flow state. This is a state characterized by relatively free movement of macromolecules or their segments in the melt relative to each other under the influence of a constant load.

Analyzing the influence of the amount of ATH on the regularity of changes in thermomechanical curves, it becomes obvious that with an increase in the filler content, a certain slowdown in the deformation process in the region of the viscous



flow state is observed. Analysis of the given thermomechanical curves shows that the studied composites based on PP-R/ATH are characterized by two defined regions: solid and viscous-flow. With an increase in ATH concentration from 1.0 to 50 wt. %, the softening onset temperature increases from 128 °C to 146 °C (Table III).

TABLE III. Dependence of softening temperature on the content of PP-R/ATH based composites

Amount of ATH	Softening onset temperature (°C)					
Allount of ATH $(y_t, \theta_s)$	PP- PP-R/PPC-g-		PP-R/ PPH-g-	PP-R/ LIBAID		
(wt. 70)	R/ATH	MAH/ATH	MAH /ATH	T-/ATH		
0	128	136	142	135		
1	133	141	137	137		
3	133	146	147	139		
5	134	146	138	137		
10	134	146	140	136		
20	138	147	140	135		
30	138	147	137	128		
50	146	165	157	139		

Similar results were obtained in the study thermomechanical properties of PP-R/PPC-g-MAH/ATH (Fig. 4b). When introducing ATH, a noticeable shift in the softening onset temperature is observed from 136 °C to 165 °C. A slight increase in the softening onset temperature and a shift of the curves to high temperatures is explained by the fact that with PPC-g-MAH, a significantly higher adhesion interaction between the polymer and the filler is ensured. Due to increased interaction between the polymer and the filler, an interphase zone appears with structural characteristics different from those of the matrix. As a result, during heat transfer impeding the thermal movement of macromolecules and their segments, which manifests itself in a decrease in deformability and an increase in softening onset temperatures. When filling PP-R/PPC-g-MAH with ATH, deformability decreases, which may be due to increased adhesive interaction between. Some distinctive features are observed in the thermomechanical curves of PCA1 and PCA<sub>30</sub> composites. This difference manifests itself mainly in the area of deformations in the temperature range from 149°C to 162°C for PCA<sub>1</sub> and from 154°C to 174 °C for the PCA<sub>30</sub> composition, which, apparently, can be associated with partial amorphization of the structure of the mixture.

The results of thermomechanical analysis showed approximately the same nature of changes in thermomechanical curves for composites based on PP-R/PPHg-MAH/ATH (Fig. 4c) and PP-R/LIBAID T-2/ATH (Fig. 4d) with PP-R/ATH. Fig. 4c shows the thermomechanical curves of PP-R/PPH-g-MAH/ATH composites. As can be seen from this figure, the tested samples are not subject to



13

deformation over a wide temperature range. Only after a temperature of 142 °C does the process of softening of the composites begin. For PP-R/LIBAID T-2/ATH composites, this temperature is equal to 135°C degree (Fig. 4d).

# CONCLUSION

In the present study, a thermophysical and thermomechanical properties study has been done for a PP-R / ATH composites with 3 types of commercial grade compatibilizers and different content of ATH. Based on the results, the following conclusions were drawn from the stud:

- 1. Thermo-physical properties of obtained composites were analyzed using differential scanning calorimetry, thermogravimetric analysis, derivative thermogravimetry and thermomechanical curves. Results from the above thermal analysis turned out that incorporation of ATH into PP-R and PP-R/compatibilizer led to improved thermal characteristics, with a lower maximum mass loss rate and higher residue.
- 2. An increase in the ATH content in the composite leads to a change in the structure of the PP-R and PP-R/compatibilizer and a decrease in its melting temperature. The melting enthalpy of composites containing compatibilizers was lower than composites without compatibilizers and this effect was associated with good interfacial adhesion and better dispersion of ATH. The difference in the effect of the type of compatibilizer on the thermal properties of the PP-R/compatibilizer/ATH composite is manifested in the higher amount of filler.
- 3. With the increase in the ATH amount, an increase in the softening temperature of the composites based on PP-R/ATH and PP-R/PPC-g-MAH/ATH was observed, while a wave-like change was observed for PP-R/PPH-g-MAH/ATH and PP-R/LIBAID T-/ATH.

## ИЗВОД

# УТИЦАЈ РАЗЛИЧИТИХ КОМПАТИБИЛИЗАТОРА И КОЛИЧИНЕ АЛУМИНИЈУМ-ХИДРОКСИДА НА ТЕРМОФИЗИЧКА И ТЕРМОМЕХАНИЧКА СВОЈСТВА КОМПОЗИТА НА БАЗИ СЛУЧАЈНОГ КОПОЛИМЕРА ПОЛИПРОПИЛЕНА И АЛУМИНИЈУМ-ХИДРОКСИДА

FATIMA MUSTAFAYEVA<sup>1</sup>, NAJAF KAKHRAMANOV<sup>1</sup>, GALINA MARTYNOVA<sup>2</sup>, NELI KOSEVA<sup>3</sup>

<sup>1</sup>Institute of Polymer Materials of Ministry of Science and Education Republic of Azerbaijan, S. Vurgun Str. 124, Sumgait, Republic of Azerbaijan, <sup>2</sup>Institute of Geology and Geophysics of Ministry of Science and Education Republic of Azerbaijan, H. Javid av. 119, Baku, Republic of Azerbaijan, and <sup>3</sup>Institute of Polymers, Bulgarian Academy of Sciences, ul. "Akad. Georgi Bonchev" 103, 1113 Geo Milev, Sofia, Bulgaria.

Ова студија истражује утицај три различита комерцијално доступна компатибилизатора (DuPont<sup>™</sup> Fusabond<sup>®</sup> P353 Polymer Modifier, Exxelor<sup>™</sup> PO 1020, LIBAID T-2) на термичка својства композита на бази случајног кополимера полипропилена и алуминијум-хидроксида (PP-R/ATH). Разматра се утицај поменутих компатибилизатора,

као и количине ATH-а, на термофизичка и термомеханичка својства ових композита. Термичка својства добијених композита анализирана су коришћењем диференцијалне скенирајуће калориметрије, термогравиметријске анализе, деривативне термогравиметрије и термомеханичких кривих.

Резултати студије показују да садржај ATH-а у PP-R матрици, како у присуству компатибилизатора, тако и без њега, значајно утиче на промене термофизичких и термомеханичких карактеристика. Са повећањем садржаја пунила, уочено је повећање количине остатка при 700 °C, температуре при максималној брзини губитка масе, температуре разлагања од 50%, као и смањење температуре почетка деградације. Утицај коришћених компатибилизатора на температуру топљења није био значајан при ниском садржају ATH-а (5 мас. %), док су при високом садржају пунила (50 мас. %) добијени различити резултати. Композити са компатибилизатором имали су ниже енталпије топљења у поређењу са онима без компатибилизатора.

(Примљено 12. новембра 2024; ревидирано 3. фебруара 2025; прихваћено 19. марта 2024.)

# REFERENCES

- 1. H. Raghuram, M. Seier, T. Koch, M. P. Jones, V.-M. Archodoulaki, *Sustain. Mater. Technol.* 8 (2023) e00745 (<u>https://doi.org/10.1016/j.susmat.2023.e00745</u>)
- F. Seidi, E. Movahedifar, G. Naderi, V. Akbari, F. Ducos, R. Shamsi, H. Vahabi, M. R. Saeb, *Polymers* 12 (2020) 1701 (<u>https://doi.org/10.3390/polym12081701</u>)
- W. Zhao, C. Kumar Kundu, Z. Li, X. Li, Z. Zhang, Compos. A: Appl. Sci. Manuf. 145 (2021) 106382 (https://doi.org/10.1016/j.compositesa.2021.106382)
- R. A. Mensah, V. Shanmugam, S. Narayanan, J. S. Renner, K. Babu, R. E. Neisiany, M. Försth, G. Sas, O. Das, *Polym. Test.* 108 (2022) 107511 (https://doi.org/10.1016/j.polymertesting.2022.107511)
- Y. Ma, L. Hu, Y. Huang, F. Chu, X. Zhang, Z. Guo, S. Jia, N. Zhu, Y. Chen, Y. Gu, Int. J. Heat Mass. Transf. 201 (2023) 123505
- (https://doi.org/10.1016/j.ijheatmasstransfer.2022.123505)
  J. Xiao, J. Hobson, A. Ghosh, M. Haranczyk, D.-Y. Wang, *Compos. Commun.* 40 (2023) 101593 (https://doi.org/10.1016/j.coco.2023.101593)
- A. P. Basnayake, J. P. Hidalgo, M. T. Heitzmann. *Construct. Build. Mat.* 304 (2021) 124540 (<u>https://doi.org/10.1016/j.conbuildmat.2021.124540</u>)
- J. Z. Liang, C. Y. Tang, Y. J. Zhang, J. Appl. Polym. Sci. 118 (2010) 332 (https://doi.org/10.1002/app.32370)
- K. Zhu, Y. Yang, C. Lin, Q. Wang, D. Ye, H. Jiang, K. Wu, ACS Omega 9(2) (2024) 2803 (<u>https://doi.org/10.1021/acsomega.3c08094</u>)
- N. Pérez, X. L. Qi, S. Nie, P. Acuña, M. J. Chen, D. Y. Wang, *Materials (Basel)* 12(1) (2019) 152 (<u>https://doi.org/10.3390/ma12010152</u>)
- 11. N. Samat, N. Zulkapali, Z. Halim, Z. Ahmad, A. I. H. D. Habibah, *Adv. Mater. Res.* 1115 (2015) 402 (https://doi.org/10.4028/www.scientific.net/AMR.1115.402)
- 12. S. Elbasuney, *Powder Technol.* **305** (2017) 538 (https://doi.org/10.1016/j.powtec.2016.10.038)
- A. ur R. Shah, D.-W. Lee, Y.-Q. Wang, A. Wasy, K. C. Ham, K. Jayaraman, B.-S. Kim, J.-I. Song, *Trans. Nonferrous Met. Soc. China* 24 (2014) s81 (<u>https://doi.org/10.1016/S1003-6326(14)63292-1</u>)

THERMOPHYSICAL AND THERMOMECHANICAL PROPERTIES OF COPOLYMER

- M. R. Parida, S. Mohanty, M. Biswal, S. N. Kayak, S. Rai, J. Therm. Anal. Calorim. 148 (2023) 807 (https://doi.org/10.1007/s10973-022-11851-1)
- F. A. Sabaruddin, N. Samat, A. I. H. D. Habibah, *Adv. Mater. Res.* 1115 (2015) 406 (<u>https://doi.org/10.4028/www.scientific.net/AMR.1115.406</u>)
- F. N. Joynal Abedin, H. A. Hamid, A. F. M. Alkarkhi, S. S. A. Amr, N. A. Khalil, A. N. Ahmad Yahaya, M. S. Hossain, A. Hassan, M. Zulkifli, *Polymers* 13(18) (2021) 3180 (<u>https://doi.org/10.3390/polym13183180</u>)
- K. Bedjaoui, R. Krache, A. Marcos-Fernández, M. Guessoum, *Mat. Res. Express* 6 (2019) 105334 (<u>https://doi.org/10.1088/2053-1591/ab38e7</u>)
- M. K. Chang, H. C. Lee, *Int. Comm. Heat Mass Trans.* 67 (2015) 21 (https://doi.org/10.1016/j.icheatmasstransfer.2015.06.016)
- R. Jeziorska, A. Szadkowska, M. Zielecka, M. Wenda, B. Kepska, *Poly. Degrad. Stab.* 145 (2017) 70 (<u>https://doi.org/10.1016/j.polymdegradstab.2017.06.007</u>)
- 20. N. Eszer, Z. Ishak, *IOP Conf. Series: Mat. Sci. Eng.*, **368** (2018) 012017 (<u>https://doi.org/10.1088/1757-899X/368/1/012017</u>)
- F. A. Mustafayeva, N. T. Kakhramanov, I. A. Ismailov, *Inorg. Mater. Appl. Res.* 13 (2022) 225 (<u>https://doi.org/10.1134/S2075113322010282</u>)
- N. T. Kakhramanov, Kh. V. Allahverdiyeva, Russ. J. Appl. Chem. 96 (2023) 441 (<u>https://doi.org/10.1134/S1070427223040079</u>)
- H. Yang, Z. Cai, H. Liu, Z. Cao, Y. Xia, W. Ma, F. Gong, G. Tao, C. Liuet, J. Polym. Sci. 58 (2020) 903 (<u>https://doi.org/10.1002/pol.20190210</u>)
- N. H. Thi, T. N. Nguyen, H. T. Oanh, N. T. T. Trang, D. Q. Tham, H. T. Nguyen, T. V. Nguyen, M. H. Hoang, J. Appl. Polym. Sci. 138(17) (2020) 50317 (https://doi.org/10.1002/app.50317)
- H.-K. Peng, X. X. Wang, T.-T. Li, C.-W. Lou, Y.T. Wang, J.-H. Lin, *Polym. Adv. Technol.* 30 (2019) 2045 (<u>https://doi.org/10.1002/pat.4637</u>)
- E. Bachtiar, K. Kurkowiak, L. Yan, B. Kasal, T. Kolb, *Polymers*. 11(4) (2019) 699 (<u>https://doi.org/10.3390/polym11040699</u>)
- 27. F. Mustafayeva, N. Kakhramanov, Kh. Allahverdiyeva, *Polyolef. J.* 11 (2024) 243 (https://doi.org/10.22063/poj.2024.35560.1326)
- S. N. Danilova, E. S. Efimova, N. N. Lazareva, A. A. Okhlopkova, A. G. Tuisov, *Polzunovskiy vestnik* 1 (2024) 197 (<u>https://doi.org/10.25712/ASTU.2072-</u> 8921.2024.01.024) (*In Russian*).
- Md. Khairul Hassan Bhuiyan, Md. Mahbubur Rahman, Md. Forhad Mina, Muhammad Remanul Islam, Md. Abdul Gafur, Afia Begum. *Compos. - A: Appl. Sci. Manuf.* 52 (2013) 70 (<u>https://doi.org/10.1016/j.compositesa.2013.05.011</u>).

-

15